Comparison of Field and Laboratory Methods for Detection of Arsenic at Low to Moderate Levels

Presented by

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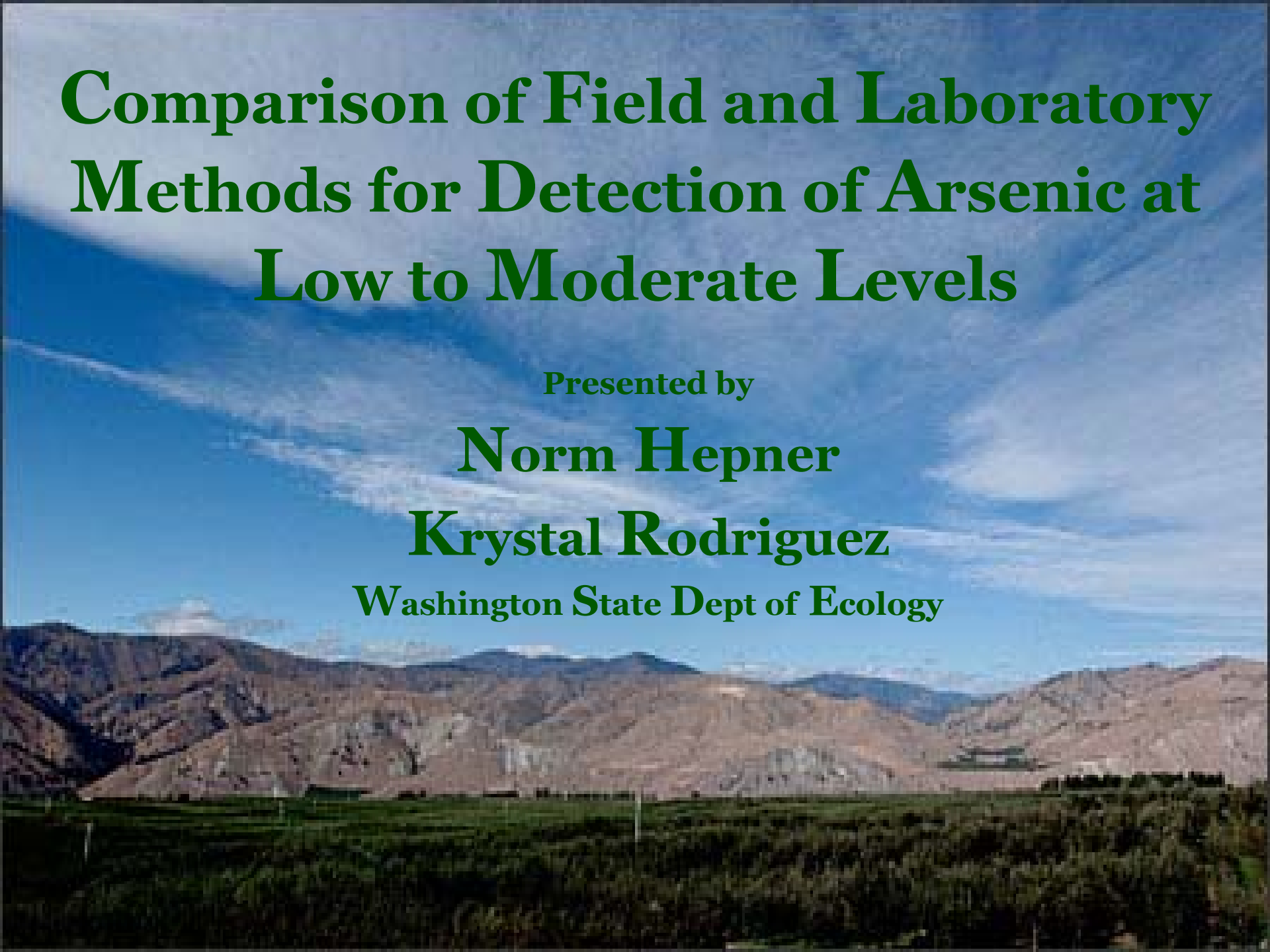


Topics

- Lead Arsenate Use in Washington State
- Purpose, Location, & Correlation
- Sampling Methods
- Analytical Methods
- Results
- Discussion
- Summary

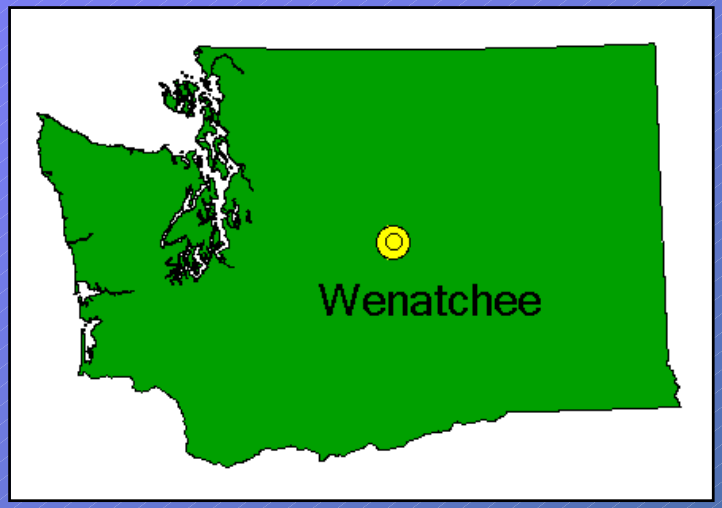
History of Lead Arsenate Use

- 1905 – Introduced in WA to fight codling moth
- 1940's – DDT introduced
- Late 1960's – Use virtually stopped in WA
- 1988 – Lead arsenate banned for use on food crops

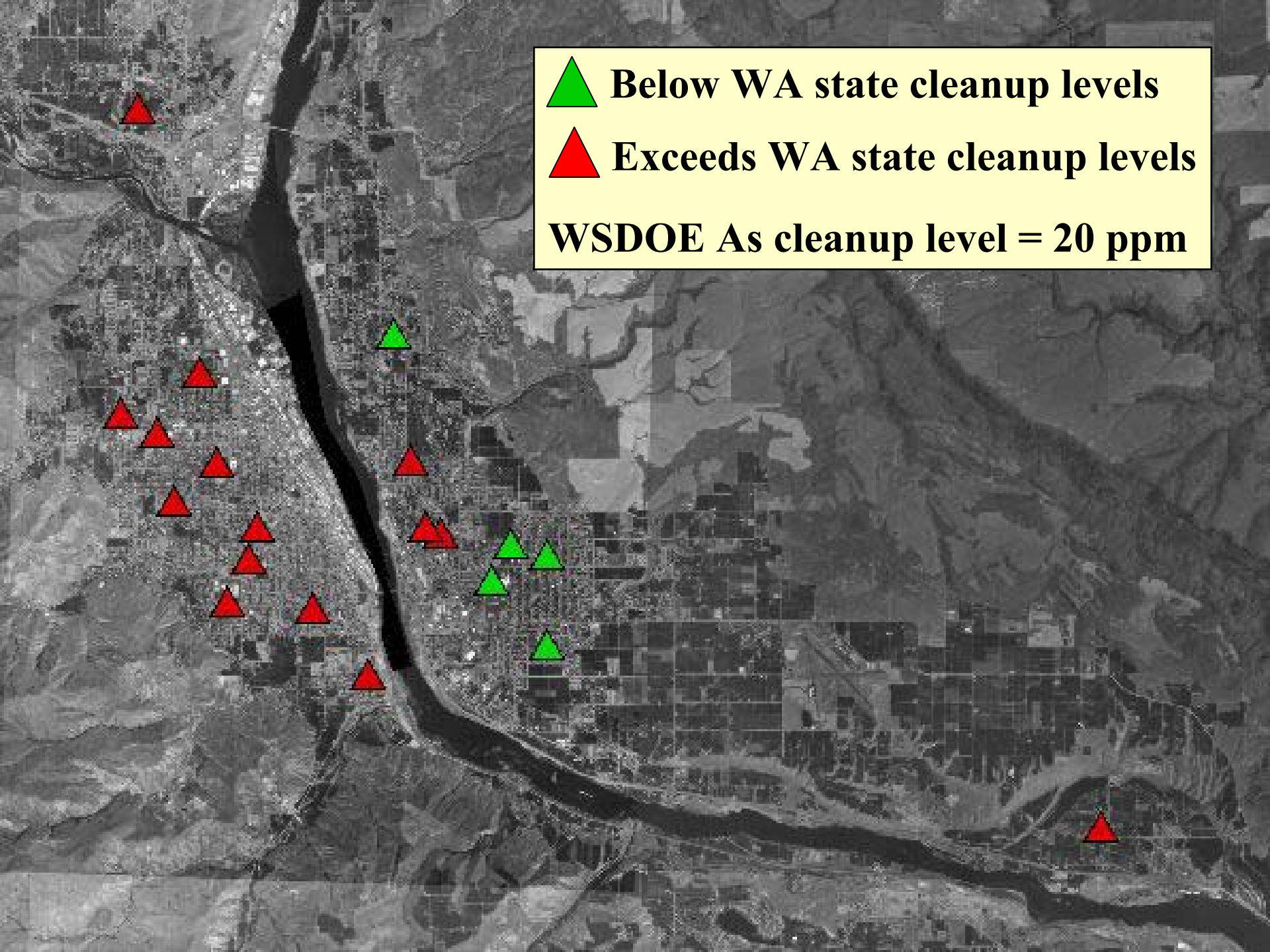
Study Background

- Received EPA Region 10 grant for analytical costs for study
- Creative settlement provided 150 FREE samples
- Yakima Area-Wide Study cancelled
- XRF and “inexpensive” Colorimetric method available

Sample Collection Area



- Wenatchee and East Wenatchee, WA
- School grounds
- Selected 100 samples
- Ranged from non-detect to 340 ppm arsenic

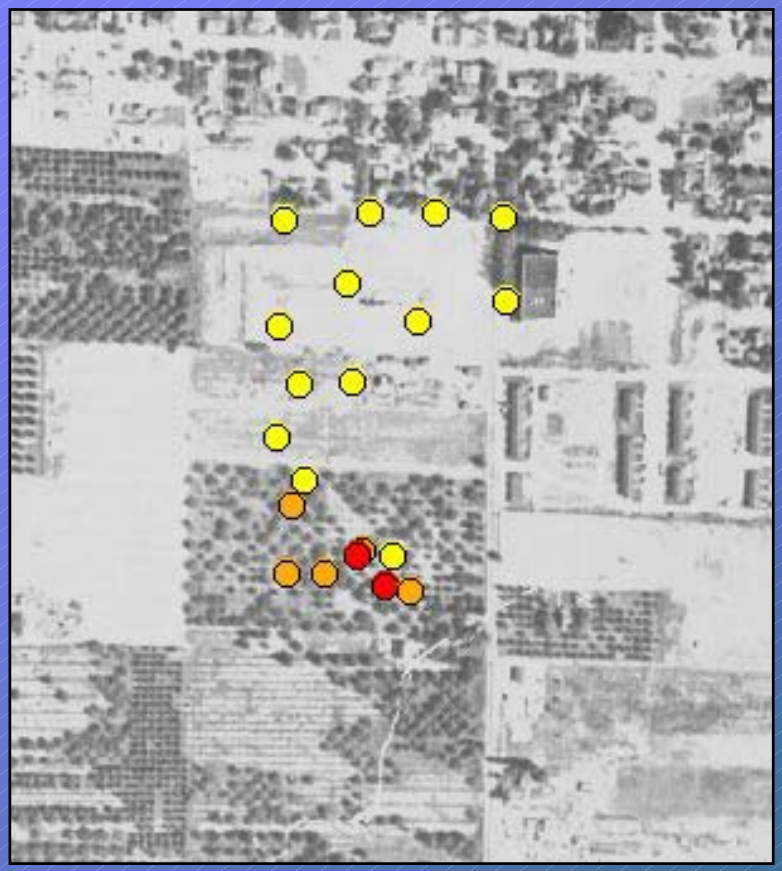

Below WA state cleanup levels
Exceeds WA state cleanup levels
WSDOE As cleanup level = 20 ppm

Correlating 1949 Orchard Land Use and Contaminant Concentrations

LIMITATIONS

- Used available 1949 aerial photo to determine land use
- Only 18 of 20 school properties in available aerial photo
- No attempt made to determine pre-1949 land use.
- Any portion of property in orchard classified as orchard.

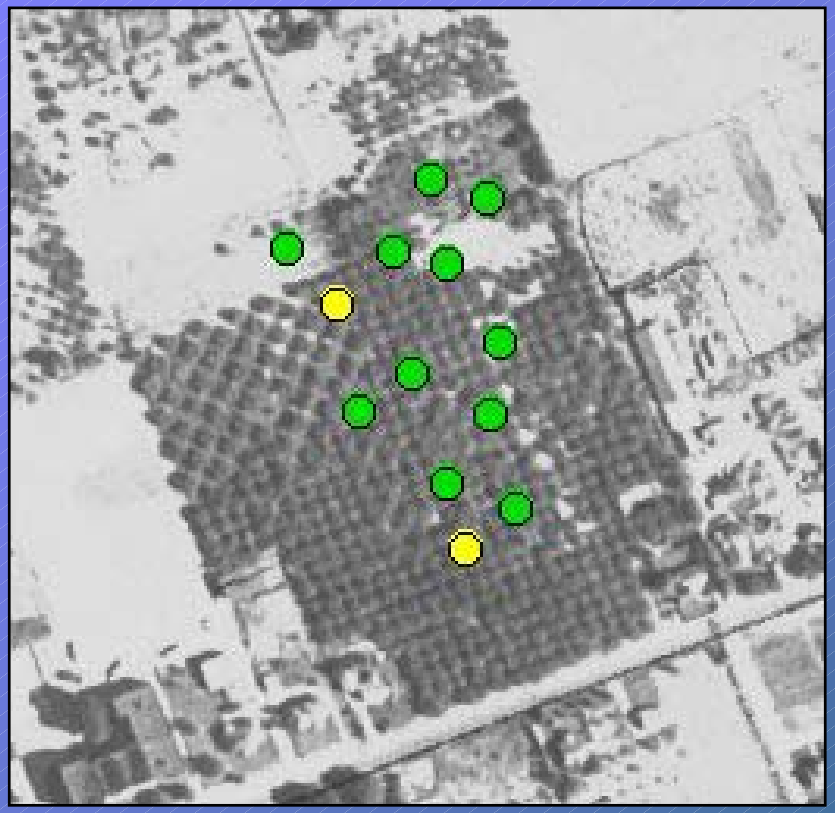
Lincoln Elementary School



1949

1998

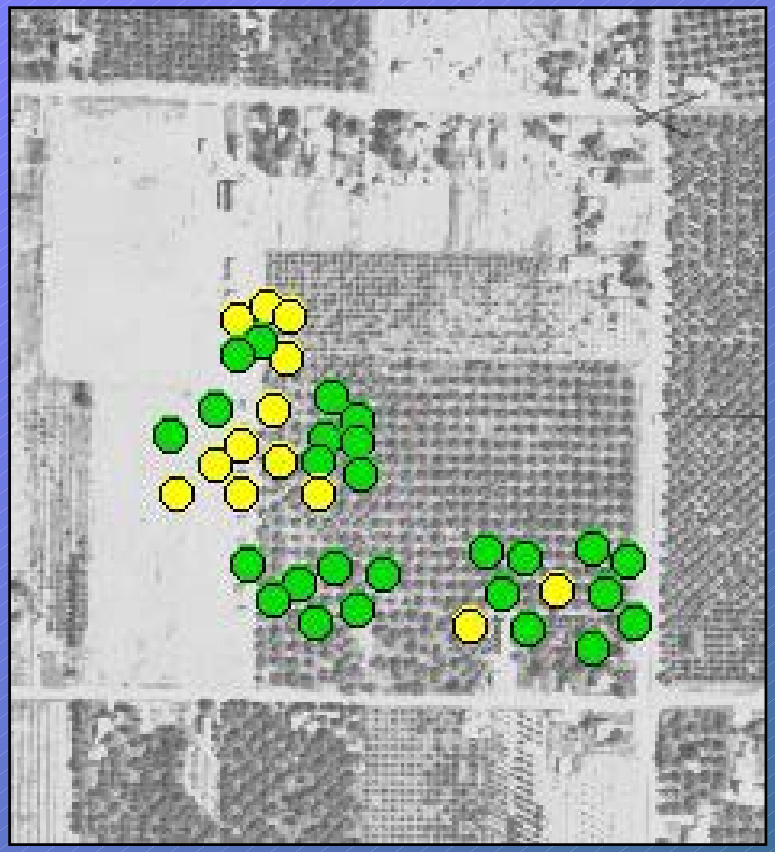
Eastmont Junior High School



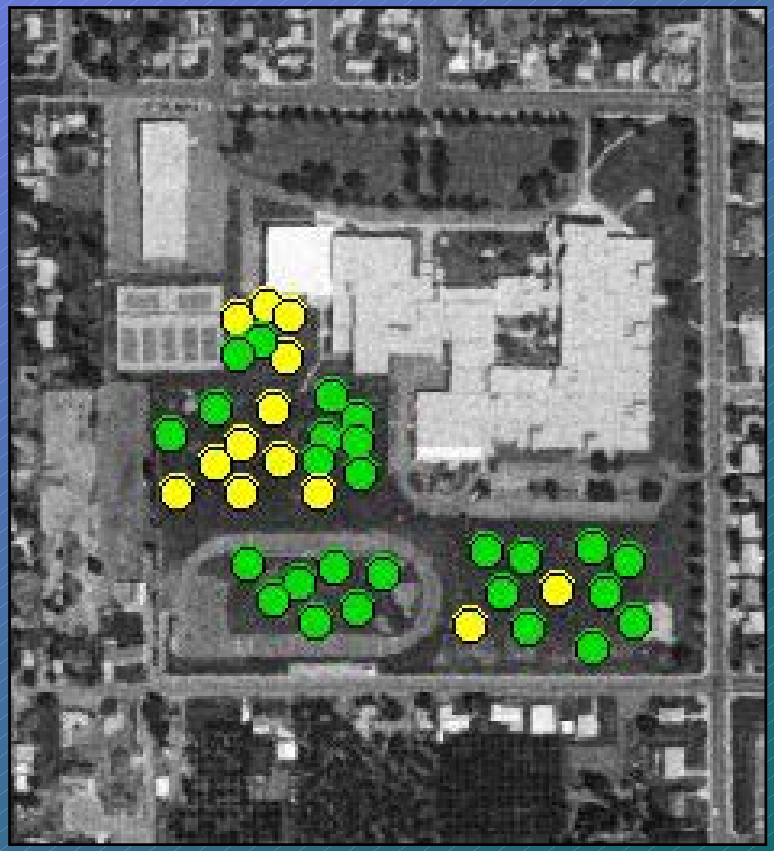
1949

1998

Wenatchee High School



1949



1998

Correlating 1949 Orchard Land Use and Contaminant Concentrations

- **RESULT:** Poor Correlation
- 11 properties above MTCA limits, 6 were not 1949 orchards.
- 7 properties below MTCA limits, 2 were 1949 orchards.

- **THEORIES:** Pre 1949 orchard use, imported or exported fill, significant property grading, nonuse or discontinuation of lead/arsenate pesticide use prior to contaminant concentrations exceeding MTCA limits.

Sample Collection

- Collected 0-6” layer of soil beneath grass layer, when present
- Removed rocks and organic debris

- Mixed soil until homogenous
- Sample placed in plastic bag and lab container.

Analytical Methods

- Niton X-ray Fluorescence (XRF)
  - Field
  - Laboratory
- Colorimetric Method
- Graphite Furnace Atomic Absorption (GFAA)
- Inductively-Coupled Plasma (ICP)
  - Standard reference method

Niton XRF

EPA Method 6200

- Uses x-ray fluorescence (XRF) to detect metals
- Cadmium-109 radioactive source
  - Quantifies 21 elements (ex. Iron, lead, arsenic, chromium, mercury, silver, etc.)

Field Niton Method

- Not dried
- Soil placed in plastic bag
- Analyzed for 400 Nsec (about 10 minutes)
  - Niton seconds (Nsec) are adjusted for radioactive source decay
  - Nsec are **not** real time

Lab Niton Method

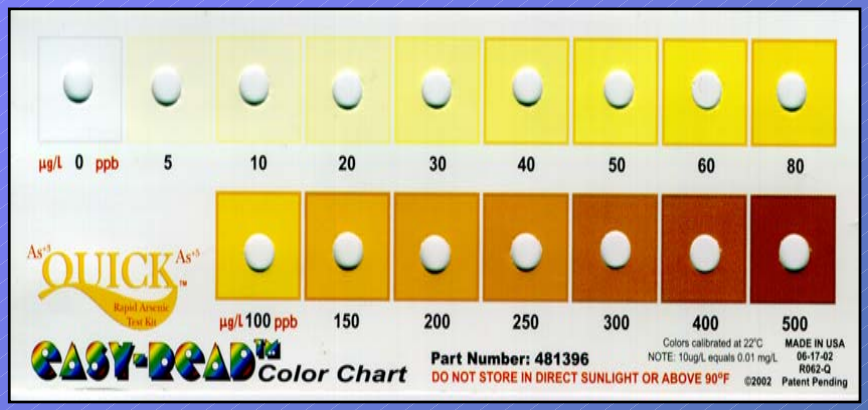
(EPA Method 6200)

- Dried soil
- Ground until about 90% of the material passed through a 250µm sieve
- Placed soil in XRF cup
- Analyzed for 400 Nsec

Colorimetric Method

Arsenic Quick™ Test Kit

by Industrial Test Systems, Inc.

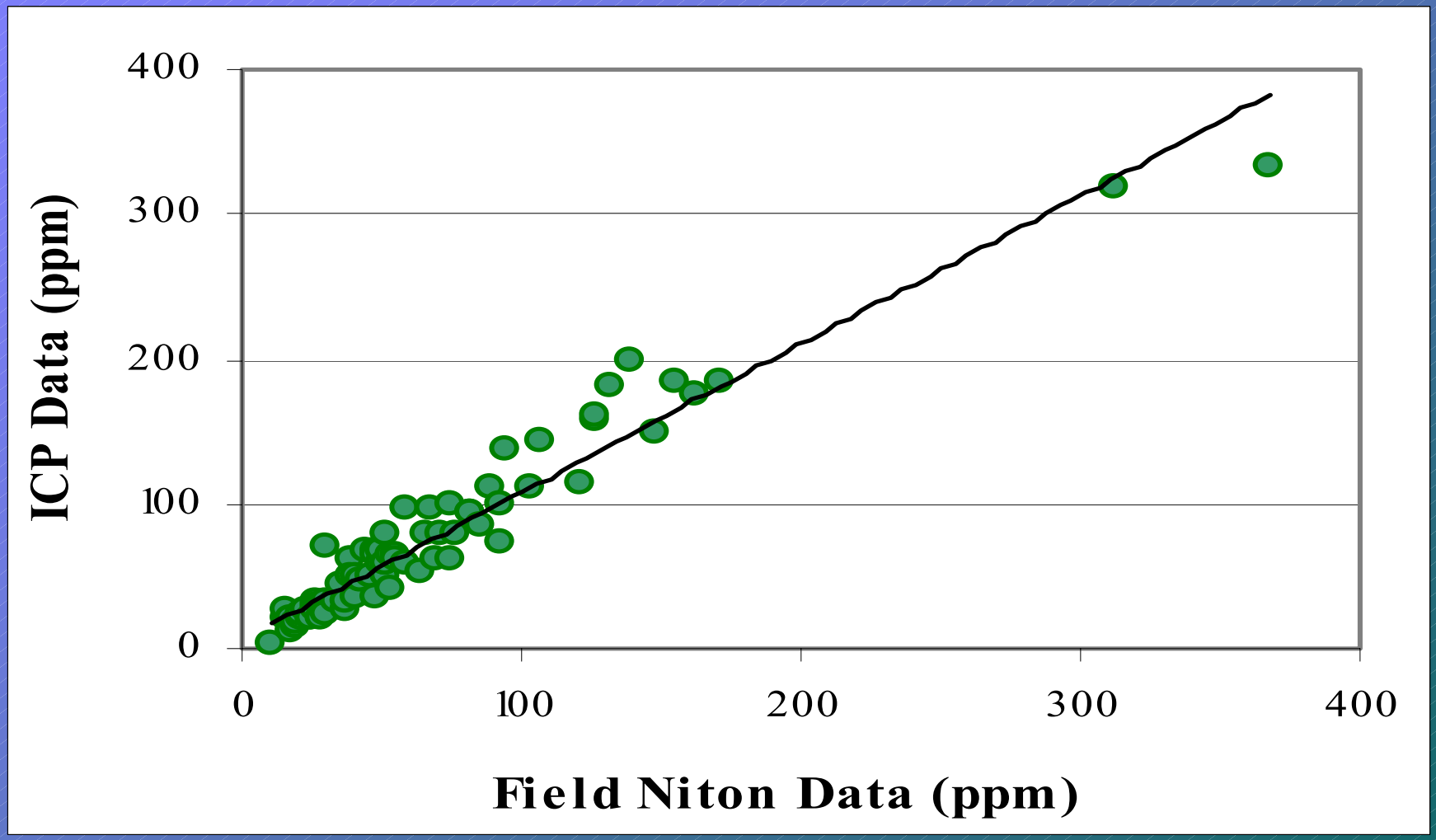


- Dried soil digested in HCl and heated to 95° C
- After cooling, sample diluted with DI water
- Reagents added to solution
- If arsenic present, arsine gas produced
- Mercuric bromide indicator strip placed in reaction tube

Laboratory Analyses

- Inductively-Coupled Plasma (ICP)
  - EPA Method 6010B
- Graphite Furnace Atomic Absorption (GFAA)
  - EPA Method 200.9
  - 20% of samples for confirmation

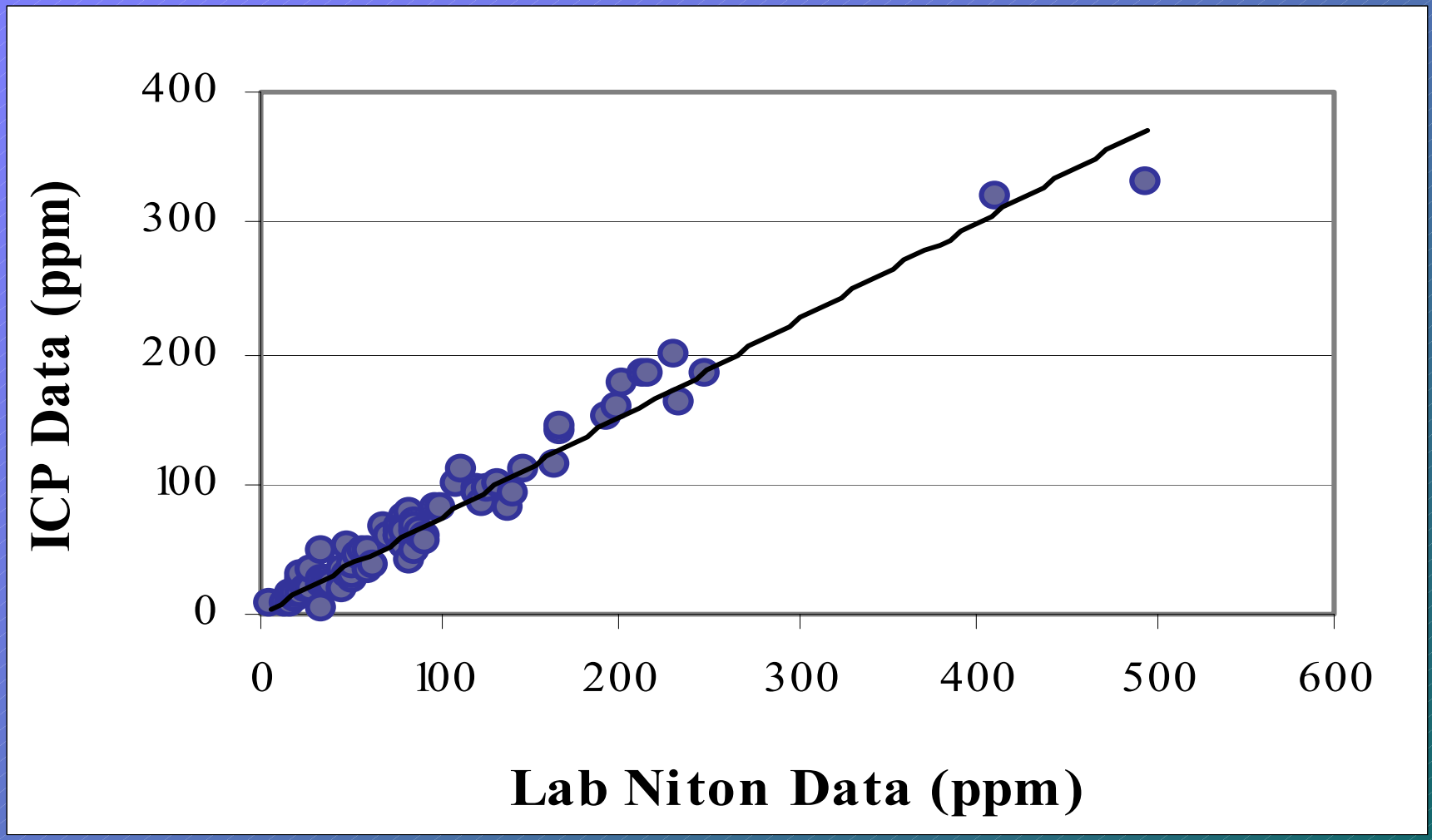
Field Niton Results



$R^2 = 0.932$

77 samples

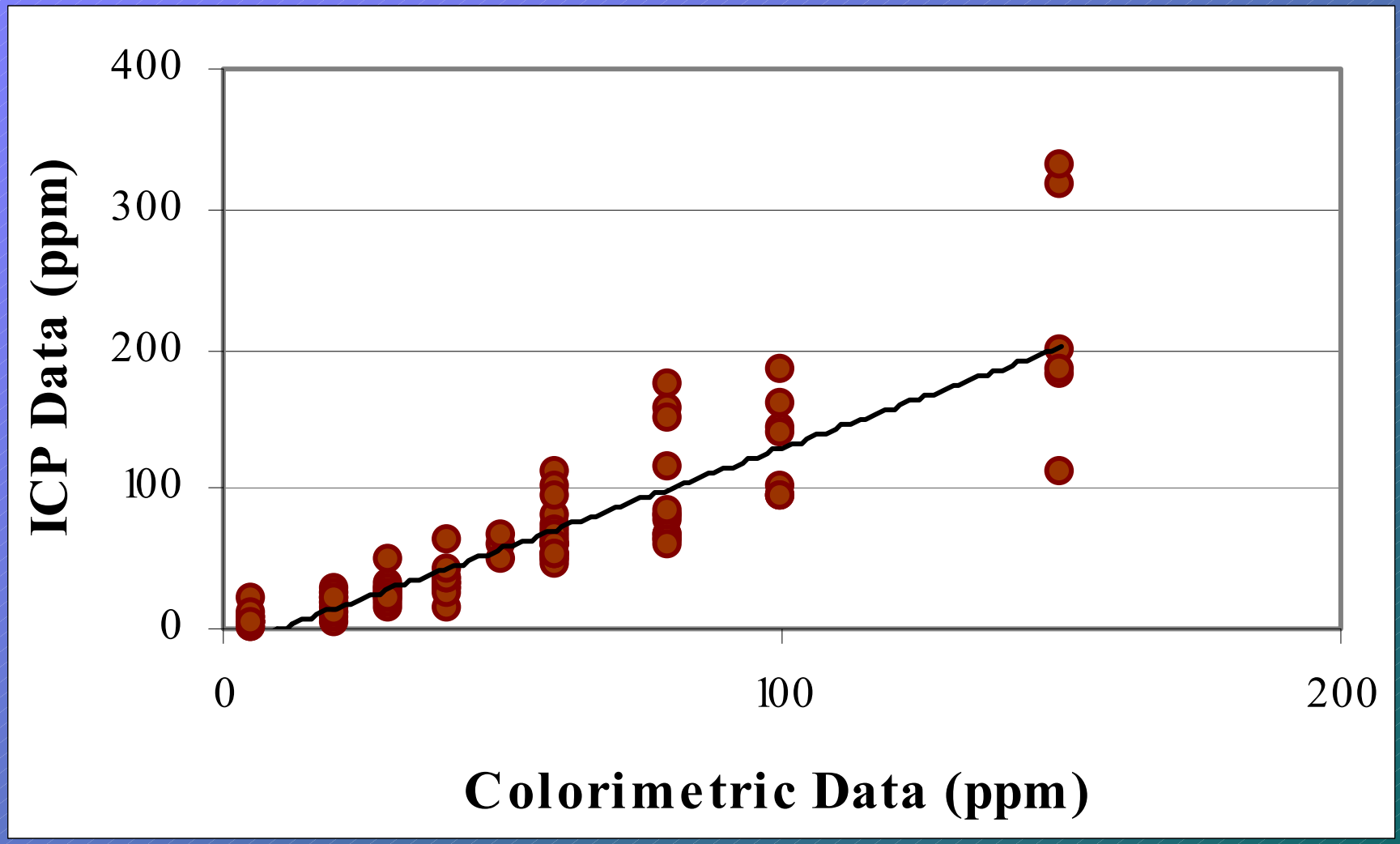
Lab Niton Results



$R^2 = 0.965$

84 samples

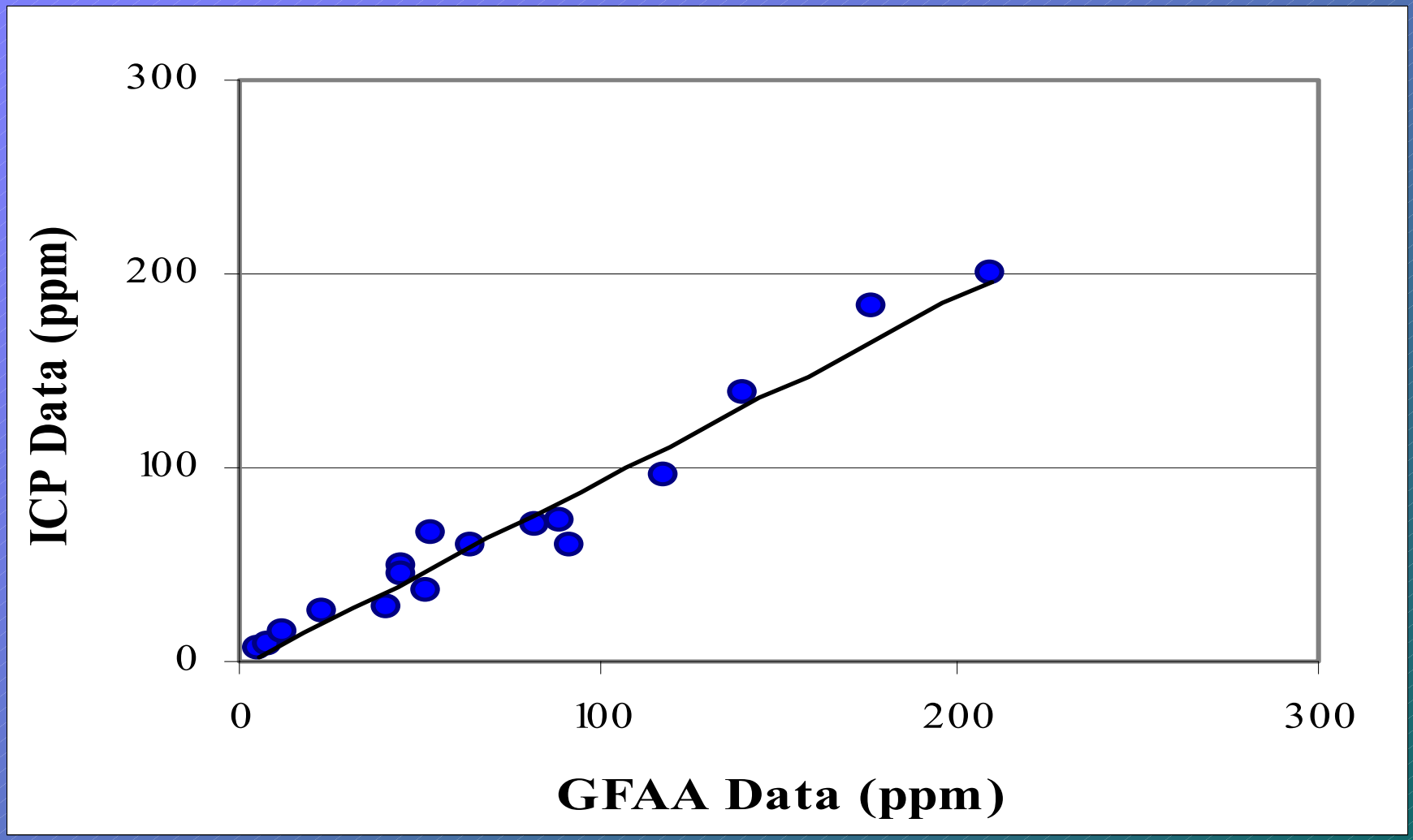
Colorimetric Results



$R^2 = 0.777$

97 samples

GFAA Results



$R^2 = 0.964$ 18 samples

Discussion

Niton XRF

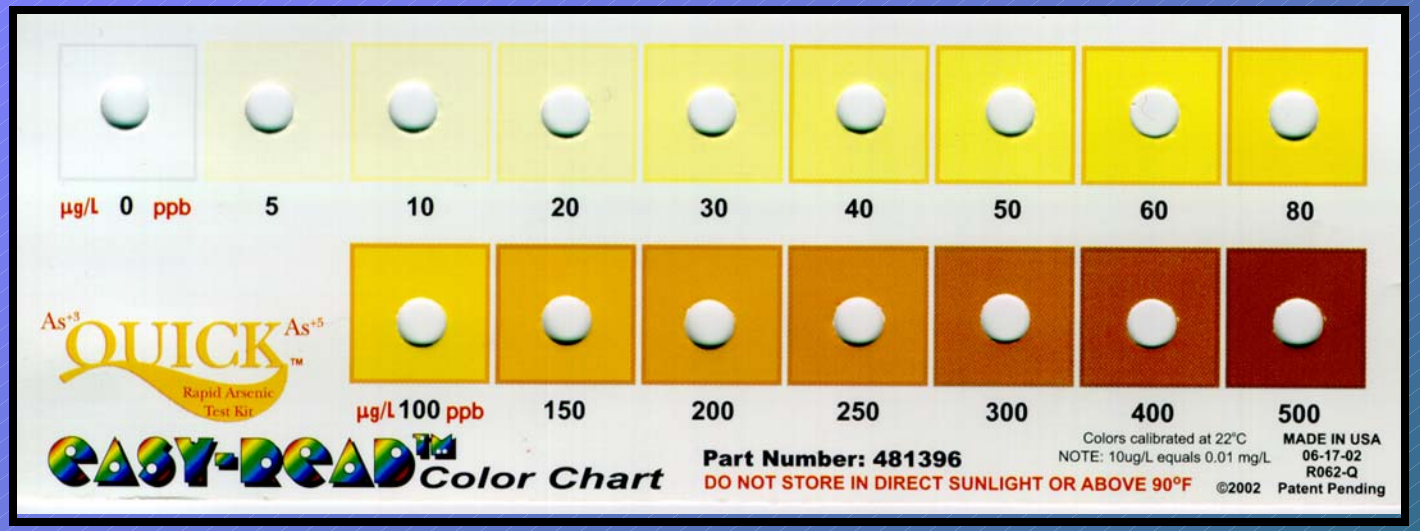
- Unlimited site characterization
  - Great for remedial activities - instant verification
- Easy to use
  - Lab Niton method more time consuming than Field Niton

Niton XRF

(cont.)

- Interferences
  - Moisture (> 20%)
  - Presence of lead at >10:1 ratio with arsenic
  - Varying particle size
  - Homogeneity
  - Organic matter

Colorimetric Method



- Lab prep work is time consuming (15 min./sample)
- Color chart doesn't allow for accuracy
- Interferences cause low As results
  - > 9,000 ppm Fe
  - > 1500 ppm Pb

Laboratory Analyses

- EPA approved methods
- Simple and easy
- Accepted and defensible in court of law
- “Limited” or “blind” site characterization

Summary

Method	Costs[a]	Turn Around Time[b]	Reliability
Field Niton	Instrument - $28,000 Cd^{109} replacement - $1,500	<10 minutes	$R^2 = 0.932$
Lab Niton	Instrument - $28,000 Cd^{109} replacement - $1,500	<40 minutes[c]	$R^2 = 0.965$
Colorimetric	$300/kit for 100 samples	2 ½ hours[c]	$R^2 = 0.777$
ICP	$25-50 / sample	2 weeks	N/A
GFAA	$25 - 50 / sample	2 weeks	$R^2 = 0.964$

a: Does not include labor costs for sample preparation time

b: Includes sample preparation time

c: Does not include sample drying time

Acknowledgements

EPA

Industrial Test Systems, Inc.

City of Yakima, WA

Lessons Learned

Niton

- Did not warm up instrument as recommended
- Lab analyzed a split sample
- 8 samples with ≥20% moisture content
  - R^2 increased by 0.015
- 2 samples with >10:1 ratio for lead and arsenic
  - R^2 decreased by 0.0002

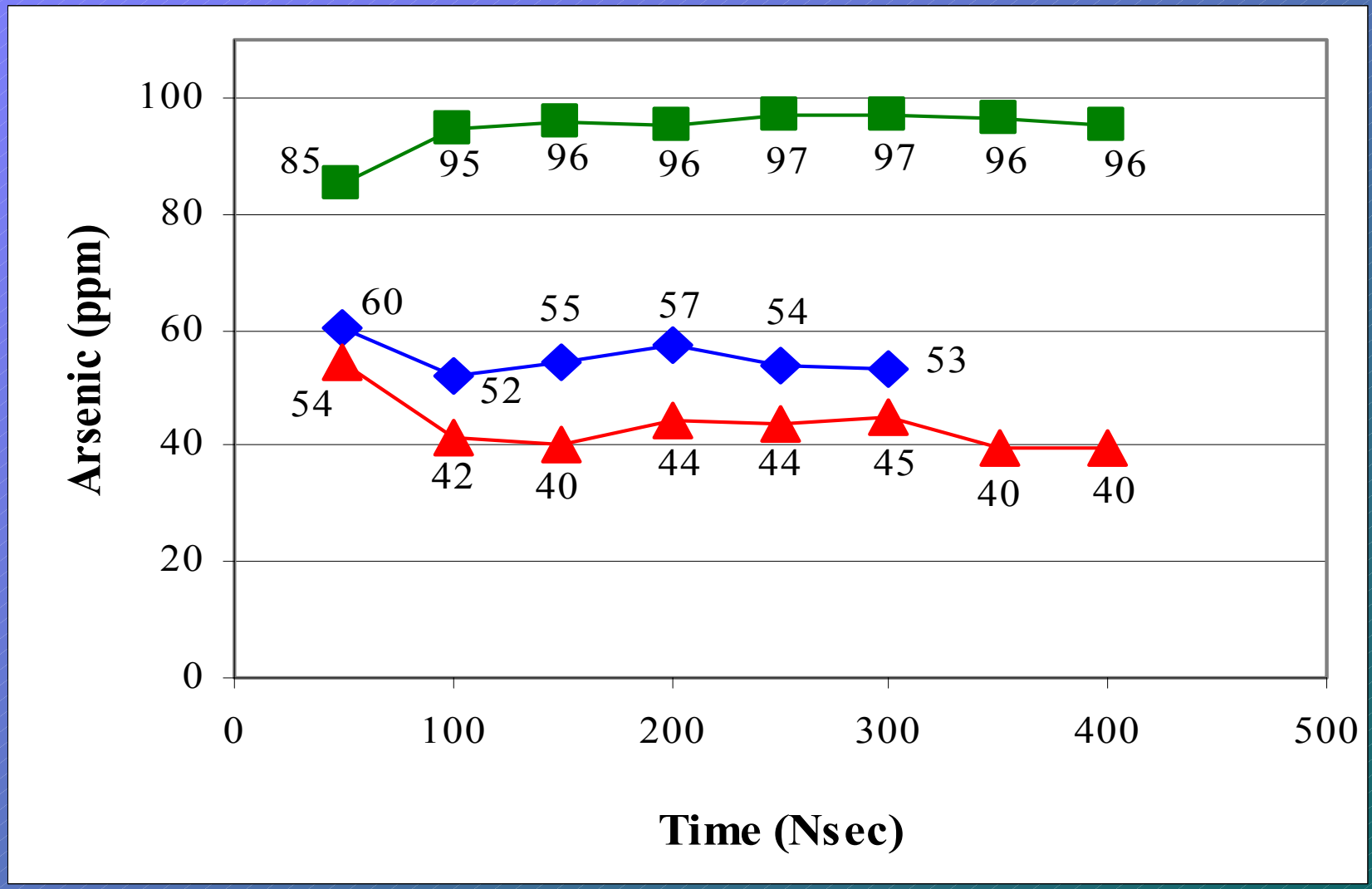
Lessons Learned

(cont.)

Niton (cont.)

- Several samples not included in statistical analysis
  - Niton results less than Level of Detection (<LOD)
  - LOD did not exceed 20 ppm
  - WSDOE cleanup level
- 400 Nsec a bit long

Niton Results vs. Nsec



Lessons Learned
(cont.)

ICP

- Two laboratories: each performed about half of the analyses
- Two different digestion methods (3050A & B)

Colorimetric

- Two staff members read color chart - subjective
- **All** samples had > 9,000 ppm Fe
- 2 samples had > 1500 ppm Pb